Stability and Structure of Transition-metal Complexes of Azoles in Aqueous Solutions. Part 21.† A Comparison of the Complex-forming Capacity of 1,2-Dimethylimidazole with that of Other 1,3-Diazoles

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Stability constants have been determined for 1,2-dimethylimidazole (dmim) complexes of Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} by a potentiometric method. Both tetrahedral and octahedral compounds are formed in the series $[Co(OH_2)_n(dmim)_x]^{2+}$ in aqueous solutions. The configurational equilibrium octahedron $\rightleftharpoons$ tetrahedron has also been found for Zn^{II}.

In previous articles the complex-forming properties of a variety of alkylimidazoles with respect to Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} have been reported.[1-5] Each of the ligands exhibited a strong tendency to form complexes. Some of the ligands formed both tetrahedral and octahedral species with Co^{II} and Zn^{II} in aqueous solution, giving rise to conformational equilibria of the type octahedron $\rightleftharpoons$ tetrahedron. The occurrence of four-co-ordinate cobalt(II) and zinc(II) complexes with certain imidazoles in aqueous solution has been confirmed by extraction studies.[6]

The previously accumulated evidence allows an evaluation of the effect of the methyl group on the complex-forming capacity of the imidazole ring and on its tendency to form tetrahedral complexes. To provide a sounder base for the discussion, the stability and structure of the 1,2-dimethylimidazole (dmim) complexes have now been studied. The complexes formed by this ligand in the solid state have been studied previously.[7-10] The authors made efforts to elucidate the geometrical structure of complexes of the type $[M(dmim)_n(anion)_2]$, where $2 \leqslant n \leqslant 4$ and $M = Mn^{II}, Fe^{II}, Co^{II}, Cu^{II}, Zn^{II}$, or Cd^{II}, which was dependent on the nature and size of the anion. The anions studied were halides, perchlorate, and tetrafluoroborate. Sundberg and Martin [11] pointed out that the co-ordination properties of the imidazole ring are greatly affected by a tendency to form both π and σ metal-ligand bonds. The present work has attempted to estimate the effect of the methyl group upon the π-acceptor properties of imidazoles and upon the tendency of the compounds to form tetrahedral species.

EXPERIMENTAL

Reagents.—1,2-Dimethylimidazole (Merck–Schuchardt) was purified by vacuum distillation. Solutions of the ligand were prepared from weighed samples. The preparation of the remaining solutions was described previously.[1,3] Ready-to-use S1326 buffer solutions of pH 7.00 ± 0.01 and 4.01 ± 0.01 (S1316) were supplied by Radiometer, Copenhagen.

Instrumentation.—A digital PHM-64 pH meter (Radiometer) and a GK 2301 combination electrode were used. The temperature was held constant at 25 ± 0.1 °C. Absorption spectra were obtained on a Beckman 25 recording spectrophotometer using 1- and 0.1-cm quartz cuvettes.

Procedure.—The stability of the complexes of Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} with 1,2-dimethylimidazole (dmim) was studied by the potentiometric method. A constant metal or ligand concentration was obtained in a given series of measurements by mixing solutions of known concentrations. The procedures and the method of determination of the dissociation constant of the protonated form of the ligand have been reported elsewhere.[2,3] For each of the ligands a series of measurements was made at three fixed metal-ion concentrations (1×10^{-2}, 2×10^{-2}, and 5×10^{-2} mol dm^{-3}). The complexes of Co^{II}, Ni^{II}, and Cu^{II} were also investigated by the spectral method over the visible range. Solutions for these measurements were prepared in a similar manner to those for potentiometric measurements at a fixed metal concentration.

All measurements were run at a constant concentration of the ligand nitrate (0.2 mol dm^{-3}) and ionic strength (0.5 mol dm^{-3} with $K[NO_3]$), at 25 ± 0.1 °C.

Calculations.—Stability constants of the complexes of Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} with dmim were determined graphically.[12] Independently, the β_n constants for the copper(II) and nickel(II) complexes were determined from the $\bar{n}$ and [L] variables by an approximation of the $\bar{n}/L] = f([L])$ function using an appropriate polynomial. The approximation was accomplished by the least-squares method on a ODRA 1013 digital computer. Values of the stability constants obtained by the two methods were comparable. To check the reliability of the equilibrium constants, the $\bar{n}$ values for a few equilibrium ligand concentrations were calculated from equation (1) by substituting the β_n values. Points determined from the co-ordinates $\bar{n}$ and pL were located on the experimental curve of $\bar{n} = f(p[L])$, thus confirming the reliability of the β_n values.

$$\bar{n} = \sum_{n=1}^{N} n\beta_n[L]^n \sum_{n=0}^{N} \beta_n[L]^n \qquad (1)$$

RESULTS AND DISCUSSION

Nickel(II) *Complexes.*—The co-ordination process in the system Ni^{II}–dmim in a nitrate solution is characterised by the formation curve shown in Figure 1. The shape of the curve suggests successive displacement of water molecules from the co-ordination sphere of the central ion by the ligand, the basic structure being retained [equation (2) where L = dmim].

$$[M(OH_2)_6]^{2+} + nL \rightleftharpoons [M(OH_2)_{6-n}L_n]^{2+} + nH_2O \qquad (2)$$

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† Part 20, is ref. 15.

The final species, whose existence can be proven, is $[Ni(OH_2)_3(dmim)_3]^{2+}$. Stability constants for particular steps of the complex formation are listed in the Table. Retention of the six-co-ordination of the Ni^{II} has also been confirmed by the results of the spectrophotometric investigations. In the absorption spectra, maxima typical for octahedral species occurred at 26 500 cm^{-1} $[^3A_{2g}\rightarrow{}^3T_{1g}(P)]$ and at 15 000 cm^{-1} $[^3A_{2g}\rightarrow{}^3T_{1g}(F)]$.

Cobalt(II) *Complexes*.—Cobalt(II) forms intensely blue-violet complexes with dmim. The spectrophotometric evidence (Figure 2) reveals that, besides pseudo-octahedral species, four-co-ordinated species also occur in solution. This is supported by the positions of the maxima and a high value of the mean molar absorption coefficient, $\varepsilon_{570} = 430$ dm^3 mol^{-1} cm^{-1} at $c_{Co} = 1 \times 10^{-3}$ and $c_L = 1.99 \times 10^{-2}$ mol dm^{-3} (curve B in Figure 2). Consequently, the spectrum in Figure 2 comprises the sum of two different bands, a weak one (at 20 000 cm^{-1}) characteristic of the octahedral cobalt(II) complexes $[^4T_{1g}(P)\rightarrow{}^4T_{1g}]$ and a much stronger band (at 17 500 cm^{-1}) typical of tetrahedral cobalt(II) compounds $[^4T_1(P)\rightarrow{}^4A_2]$.[13]

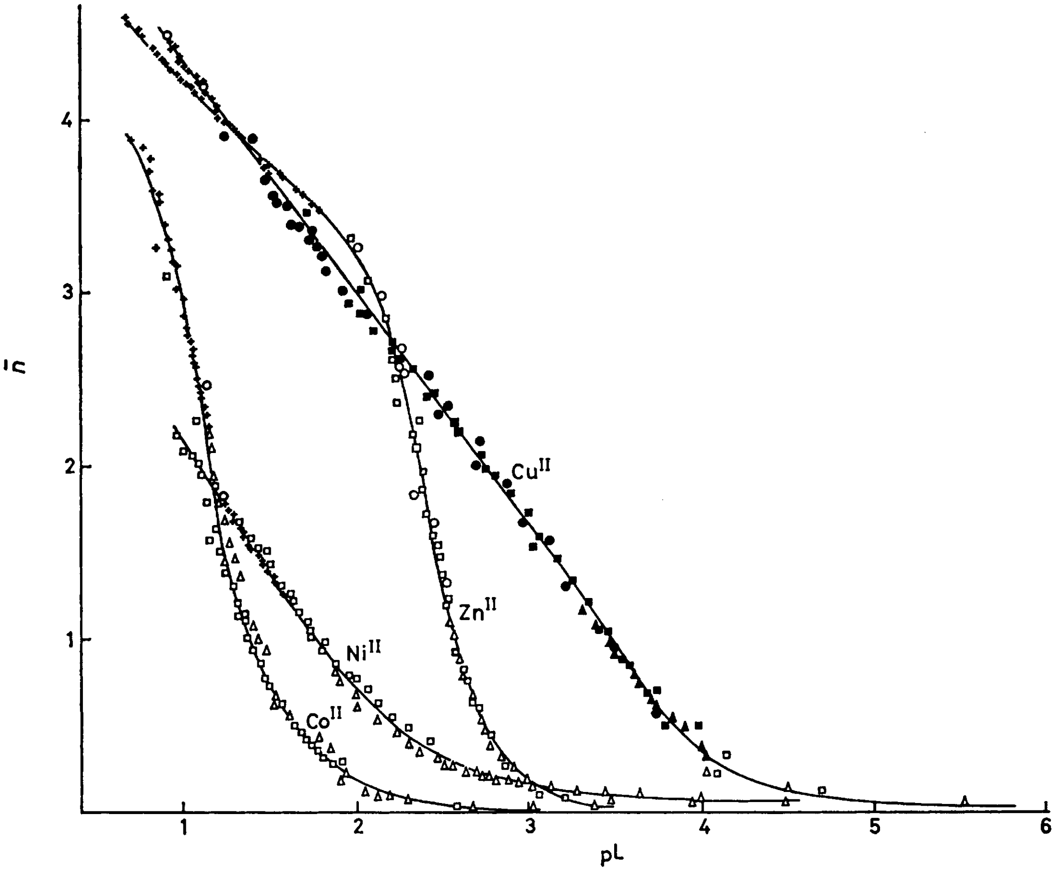

FIGURE 1 Formation curves of 1,2-dimethylimidazole complexes with Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} for three concentrations of the central ion [1 × 10^{-2} (○, ●), 2 × 10^{-2} (□, ■), and 5 × 10^{-2} mol dm^{-3} (△, ▲)] at a constant ligand concentration, and at a variable metal-ion concentration (+)

The occurrence of configurational equilibria in this system is also supported by the potentiometric measurements. The formation curve for the cobalt(II) complexes has a different shape (Figure 1) to that of the function $\bar{n} = f(p[L])$ for the nickel(II) compounds. The plot indicates that the first cobalt(II) complex exists over a relatively narrow range of the free-ligand concentration [*cf.* the almost vertical course of the curve which is similar to that of the function characterizing the zinc(II) complexes].

To get a better insight into the system the function $\bar{n}/[L] = f(\bar{n})$ was plotted (Figure 3). The shape of this curve is completely different from that for systems in which only six-co-ordinate species occur. The maximum in the curve may be due to the formation of two complexes containing three ligand molecules, $[Co(OH_2)_3L_3]^{2+}$ and $[Co(OH_2)L_3]^{2+}$.

Copper(II) *Complexes*.—Solutions containing Cu^{II} and dmim are intensely dark blue. The complexation in solution is accompanied by a large shift of the maxima in the absorption spectra towards shorter wavelengths, from *ca.* 12 500 to *ca.* 16 670 cm^{-1}, and approximately six-fold increase in the mean molar absorption coefficient, $\varepsilon_{650} = 64$ dm^3 cm^{-1} mol^{-1} at $c_{Cu} = 2 \times 10^{-2}$ and $c_L = 8.4 \times 10^{-2}$ mol dm^{-3}.

A potentiometric formation curve is shown in Figure 1. Comparison of this curve with those for complexes of the remaining metals reveals that the copper(II) com-

TABLE

Stability constants of methylimidazole complexes in aqueous solution at 25 °C and I = 0.5 mol dm^{-3} (K[NO$_3$]). The errors in the determination of the stability constants are *ca.* 10%

Ligand	pK_a [a]	Central ion	log β_1	log β_2	log β_3	log β_4	log β_5	log β_6	Ref.
N-Methylimidazole	7.19	Co^{2+}	2.40	4.40	5.85	6.95			
		Ni^{2+}	3.05	5.95	7.61	9.13			2
	7.21 [b]	Zn^{2+}	2.70	4.80	7.41	9.32	10.23		
		Cu^{2+}	4.30	7.94	10.96	13.33	14.93		
			4.22	7.76	10.65	12.86			*b*
2-Methylimidazole	8.05	Co^{2+}	1.73	3.05	3.84	6.16			
		Cu^{2+}	3.35	6.38	9.23	11.92	14.45		1
		Zn^{2+}	1.88	3.99	7.49	9.32			
4-Methylimidazole	7.80	Co^{2+}	2.34	4.09	5.33	6.67			
		Ni^{2+}	2.92	5.26	7.03	8.26			4
	7.69	Zn^{2+}	2.48	5.06	7.74	10.52	12.62	13.66	
			2.44	4.97	7.61	9.99			*c*
		Cu^{2+}	4.13	7.62	10.49	12.49			
1,2-Dimethylimidazole	8.21	Co^{2+}	1.13	2.39	3.81	4.32			This work
		Ni^{2+}	2.15	3.55	4.24				
		Cu^{2+}	3.70	6.80	9.18	10.80	11.72		
		Zn^{2+}	1.92	4.32	7.11	9.00	9.62		

[a] The Table comprises exponents of the acid-dissociation constants extrapolated to the same free-ligand concentration. [b] N. C. Li, J. M. White, and E. Doody, *J. Amer. Chem. Soc.*, 1954, **76**, 6219. [c] Y. Nozaki, F. R. N. Gurd, R. F. Chen, and J. T. Edsall, *J. Amer. Chem. Soc.*, 1957, **79**, 2123.

plexes are the most stable. It is worth noting that a plot of the function $\bar{n}$ = f(p[L]) for the Cu^{II}–dmim system does not show an inflection at $\bar{n} = 4$ due to decreased stability of the fifth and sixth complexes because of the Jahn–Teller effect. This inflection was found for copper(II) complexes of *N*-alkylated imidazoles.[5]

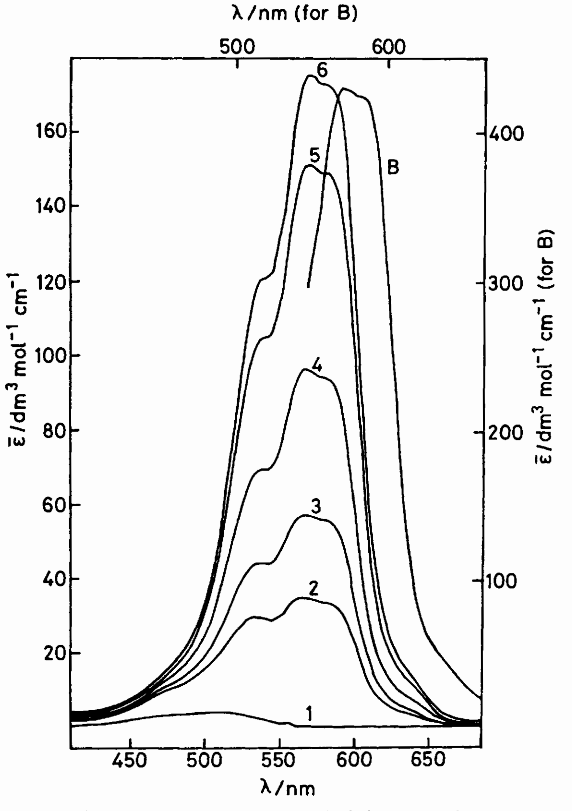

FIGURE 2 Absorption spectra of cobalt(II) complexes with 1,2-dimethylimidazole at 1 × 10^{-2} mol dm^{-3} Co[NO$_3$]$_2$. The ligand concentrations (10^{-3} mol dm^{-3}) are 0, 49.7, 63.7, 74.7, 87.6, 99.6, and 199.5 for curves 1—6 and B, respectively

Zinc(II) *Complexes*.—The shape of the formation curves obtained from potentiometric measurements suggests that in solutions of Co^{II} or Zn^{II} and dmim both four- and six-co-ordinate species occur, the former possessing a tetrahedral or pseudo-tetrahedral structure. However, the initial portion of the $\bar{n}$ = f(p[L]) curve is more steep for Zn^{II} than for Co^{II}. This may be due either to a greater stability of the tetrahedral zinc(II) complexes or to the establishment of a configurational equilibrium for the first complex.

Between the $\bar{n}$ values of 3 and 4 a distinct inflection occurs in the formation curve for Zn^{II}. This may be explained if we take into account the fact that at $\bar{n} > 4$ only octahedral species can occur in solution, which are probably less stable. This interpretation is supported by a plot of the function $\bar{n}$/[L] = f($\bar{n}$) which exhibits one distinct maximum and has a shape entirely different from that for Ni^{II}.

The Course of the Co-ordination of 1,2-*Dimethylimidazole to* Co^{II}, Ni^{II}, Cu^{II}, *and* Zn^{II}.—Figure 4 shows the relationship between the logarithms of the stability constants of the complexes of Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} with dmim and the number of ligand molecules attached. The linearity of the function log K_n = f(n − 1) for Ni^{II} and Cu^{II} is in accord with the van Panthaleon van Eck equation,[14] thus revealing that the complexation is similar in the two systems and conforms to the statistical model.

With Cu^{II}, no decrease in the stability of the fifth complex (due to the Jahn–Teller effect) is reflected in the plot of log K_n = f(n − 1). Consequently, this complex may possess a structure other than tetrahedral.

Cobalt(II) and Zn^{II} do not obey a linear relationship, revealing that their complexation is accompanied by a decrease in the co-ordination number from six to four. This leads to the establishment of the configurational octahedron $\rightleftharpoons$ tetrahedron equilibrium (3). Thus the

$$[M(OH_2)_{6-n}L_n]^{2+} \rightleftharpoons [M(OH_2)_{4-n}L_n]^{2+} + 2H_2O \quad (3)$$

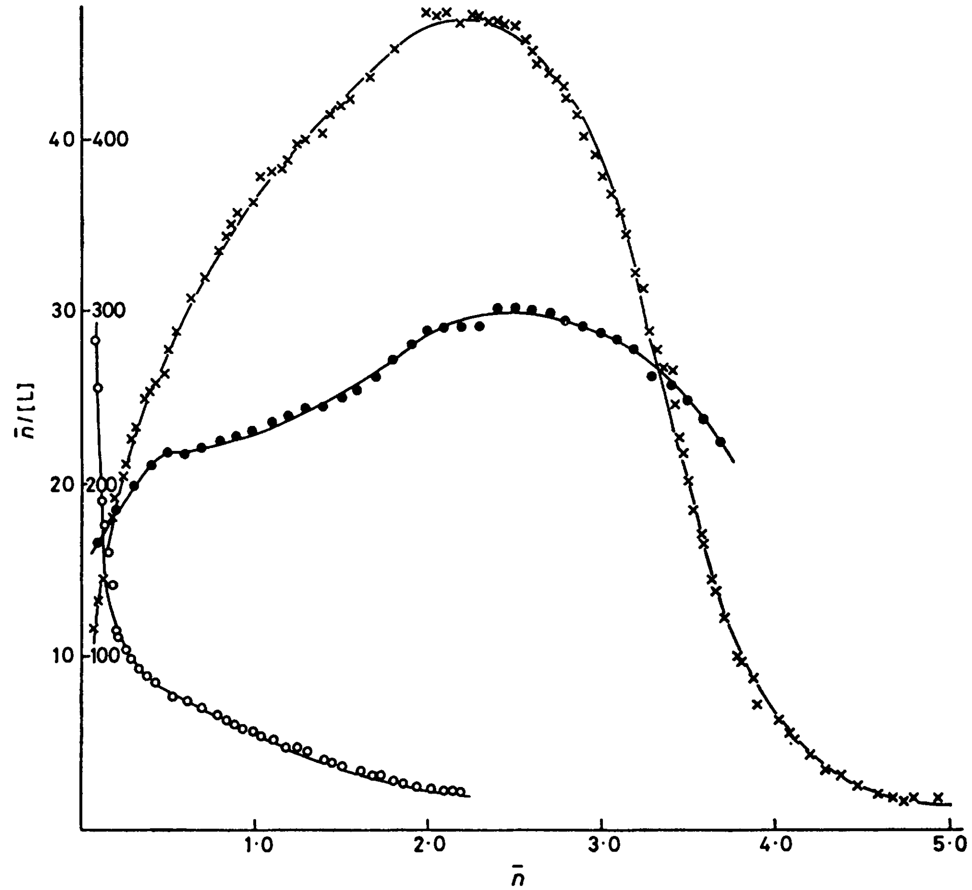

FIGURE 3 Dependence of $\bar{n}/[L]$ on $\bar{n}$ for complexes of Ni^{II} (○), Co^{II} (●), and Zn^{II} (×). The lower scale for $\bar{n}/[L]$ applies only to Co^{II}

successive stability constants characterizing the respective complexation steps (1 through 4) provide a sum of partial constants describing the stability of the octahedral and tetrahedral complexes [equation (4)], where K_n is the overall formation constant, K_n^O the formation constant of the octahedral complexes, and K_n^T the formation constant of the tetrahedral complexes.

$$K_n = K_n^O + K_n^T \quad (4)$$

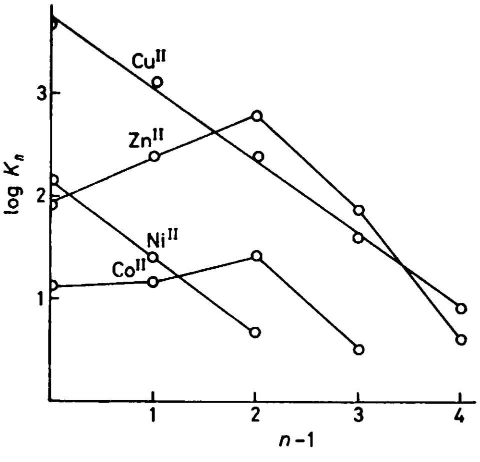

FIGURE 4 Changes in the values of the formation constants for successive complexes of 1,2-dimethylimidazole with Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}

Comparison of the Complexing Power of 1,2-*Dimethylimidazole with that of Other Methyl Derivatives of* 1,3-*Diazoles*.—Equilibrium constants for the different steps in the formation of the dmim complexes are listed in the Table together with those of previously studied methylimidazoles. Comparison of these stability constants allows conclusions to be drawn about the effect of methyl groups on the complexing power of the imidazole ring.

The basicity of imidazole is greatly increased by introduction of the methyl group in position 2, the weakest effect being observed when the group is attached to the ring nitrogen atom (position 1). For this reason, dmim has the highest basicity of all the imidazoles studied since in this case the inductive effect of two methyl groups is operating. The high basicity should favour the formation of stable complexes with transition-metal ions. However, complexation may be hindered by the adjacent methyl group. To estimate the effect of these two factors upon the stability of complexes, logarithms of the third stability constants (log β_3) were plotted against the exponents of the acid-dissociation constants of the protonated form of the ligand. As seen in Figure 5, an increase in the basicity of a 1,3-diazole results in decreasing stability of the six-co-ordinate complexes of Ni^{II}

and Cu^{II}. A similar decrease was observed with Co^{II}. However, with strong bases (2-methylimidazole, 1,2-dimethylimidazole) the values of the stability constants are almost constant owing to the predominance of tetrahedral species in solution. A different shape of the function log $\beta_3 = f(\text{p}K_a)$ has been observed with the zinc(II) complexes.

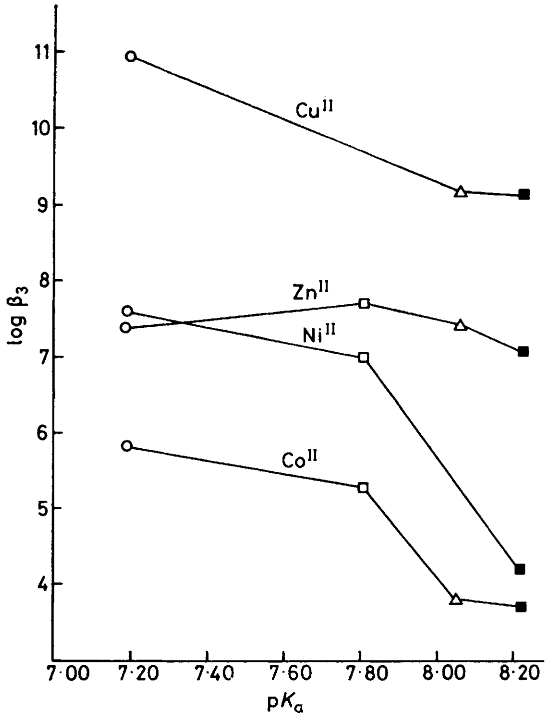

FIGURE 5 Relation between log β_3 and pK_a for *N*-methylimidazole (○), 4-methylimidazole (□), 2-methylimidazole (△), and 1,2-dimethylimidazole (■) complexes of Co^{II}, Ni^{II}, Zn^{II}, and Cu^{II}

A decrease in the complexing power of the imidazole derivatives can be explained in terms of a lowering of the π-acceptor properties of the 1,3-diazole ring owing to hyperconjugation and the inductive effect of the methyl groups. A consequent decrease in the contribution of the $\pi(M \rightarrow L)$ bonding apparently does not hinder the formation of tetrahedral species. A similar relation between the stability of complexes and the basicity of ligands has been observed for methylpyrazoles.[15]

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